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(54) **Fuel additive**

(57) Use of a carboxylic acid ester of an alkanolamine as an additive for improving the lubricity of

a low sulfur-content fuel, such as a diesel, bio-diesel or jet fuel.

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Description

The present invention relates to the use of certain compounds to improve the lubricating properties of low sulfur-content fuels and to fuels and additive concentrates comparing the compounds.

Sulfur contained in fuel for example middle distillate fuels such as diesel fuel and jet fuel, is said to constitute a serious environmental hazard. Hence strict regulations limiting the amount of sulfur which may be present in such fuels have been introduced. Unfortunately, fuels having a suitably low sulfur content exhibit very poor inherent lubricity and this can lead to problems when the fuel is used. For example, the use of low sulfur fuel in diesel engines frequently results in damage to the fuel injector pump which relies on the natural lubricating properties of the fuel to prevent component failure. There is therefore a need to improve the lubricating properties of low sulphur fuels.

It has now been found that the lubricating properties of low sulfur fuels can be improved by the use of certain additive compounds as described in detail below. This enables mechanical failure, for example fuel injector pump failure, caused by inadequate fuel lubricity to be avoided while retaining the environmental benefit of using a low sulfur fuel.

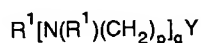
In the present context the term "low sulfur-content fuel" is intended to mean fuels typically having a sulfur content of 0.2% by weight or less, for example 0.05% by weight or less and, more especially, 0.005% by weight or less. Examples of fuels in which the additive compounds may be used include low sulfur middle distillate fuels such as diesel and jet fuels and bio-diesel fuel. The latter is derived from a petroleum or vegetable source or mixture thereof and typically contains vegetable oils or their derivatives, such as esters produced by saponification and re-esterification or transesterification. Middle distillate fuels are usually characterised as having a boiling range of 100 to 500°C, more typically from 150 to 400°C.

In accordance with the present invention the additive used to improve the lubricity of low sulfur-content fuel is a carboxylic acid ester of an alkanolamine. The ester may be used alone or in combination with other esters as described herein.

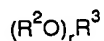
The acid used in the present invention is one which does not contain any hydroxy-substitution in the acid backbone. The acid typically contains up to 60 carbon atoms. The acid may be a mono- or poly-carboxylic acid or a dimerized acid. When mono-carboxylic acids are used they typically contain 10 to 40 carbon atoms, more commonly 10 to 30 and especially 12 to 24 carbon atoms. Examples of such include aliphatic fatty acids such as lauric, myristic, heptadecanoic, palmitic, stearic, oleic, linoleic, linolenic, nonadecanoic, arachic or behenic acid. Of these the use of oleic acid is preferred. When poly-carboxylic acids are used, such as di- or tri-carboxylic acids, they typically contain 3 to 40 carbon atoms, more commonly 3 to 30 and especially 3 to 24 carbon atoms. Examples of this kind of poly-carboxylic acid include dicarboxylic acids such as succinic, glutaric, adipic, suberic, azelaic or sebacic acid, and tricarboxylic acids such as 1,3,5-cyclohexane tricarboxylic acid and tetracarboxylic acids such as 1,2,3,4-butane tetracarboxylic acid.

It is also possible to use as the hydroxy-substituted acid, dimerized acids. Herein such compounds are referred to as dimer and trimer acids. When used the dimerized acid typically contains 10 to 60, preferably 20 to 60 and most preferably 30 to 60, carbon atoms. Such acids are prepared by dimerizing unsaturated acids and typically consist of a mixture of monomer, dimer and trimer acid. According to a preferred embodiment of the invention the acid is a dimerized fatty acid, for example of oleic and linoleic acids. Typically this dimer exists as a mixture of 2% by weight monomer, 83% by weight dimer and 15% by weight of trimer and possibly higher acids. The preferred dimer acid, as well as the other acids described above, are commercially available or may be prepared by the application or adaption of known techniques.

The alkanolamine used to form the ester used in the present invention is typically of formula:



in which p is 2 to 10, q is 0 to 10, Y is $-N(R^1)_2$, 4-morpholinyl or 1-piperazinyl N-substituted by a group R^1 or a group $-[(CH_2)_pN(R^1)]_qR^1$ in which p and q are as defined above and each substituent R^1 is independently selected from alkyl groups having from 1 to 6 carbon atoms and a group of formula:



in which r is 0 to 10, R^2 is an alkylene group having from 2 to 6 carbon atoms, R^3 is an hydroxyalkyl group having 2 to 6 carbon atoms and provided at least one group R^1 is $-(R^2O)_rR^3$. Thus, the alkanolamine is one which does not contain any hydrogen-bearing nitrogen atoms. The presence of free hydrogen atoms would be expected to lead to the formation of an amide on reaction with the fatty acid.

In the formulae for the alkanolamine p is 2 to 10, preferably 2 or 3, q is 0 to 10, preferably 0 to 5 and r is 0 to 15, preferably 0 to 10. When R¹ is alkyl it contains from 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms. R² is an alkylene group having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms. R³ is an hydroxyalkyl group having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms. The hydroxyalkyl group typically contains 1 to 3 hydroxy groups. When r is greater than zero R³ is typically a mono-hydroxyalkyl group, for example hydroxyethyl or hydroxypropyl. When r is zero R³ is typically a mono- or poly-hydroxyalkyl group having up to 4 hydroxy groups, for example hydroxyethyl, hydroxypropyl or a 1-hydroxy-2,2-bis(hydroxymethyl)ethyl group. The values p, q and r take are selected independently. This means for example that when q is greater than zero, p may take different values in each repeat unit. Also, when r is greater than zero, R² may be the same or different in each ether repeat unit.

The alkanolamines which may be used to form the ester are commercially available or may be made by the application or adaptation of known techniques. For example, the alkanolamines in which r is 1 or more, i.e. those containing an ether of polyether linkage, can be prepared by reaction of a suitable amine, morpholine or piperazine compound with a molar excess of one or more alkylene oxides. When the same kind of alkylene oxide is used R² and R³ contain the same alkylene moiety. When different kinds of alkylene oxide are used R² and R³ may contain the same or different alkylene groups.

According to a preferred embodiment, alkanolamines of the above formula are used in which Y is -N(R¹)₂, p is 2 and q is 0 to 3. Preferably the alkanolamine is triethanolamine or triisopropylamine or ethylene diamine or diethylene triamine in which each nitrogen atom is substituted by hydroxyethyl or hydroxypropyl groups.

According to an alternative preferred embodiment, in the formula shown above, Y is 4-morpholinyl or substituted 1-piperazinyl, p is 2 to 6 and q is 0 or 1. Examples of such alkanolamines include aminoethylpiperazine, bis-(aminoethyl)piperazine or morpholine, N-substituted by an hydroxypropyl group.

The esters described may be made by the application or adaptation of known techniques, or are commercially available ready for use.

According to one aspect of the present invention, the ester contains at least one free carboxylic group in the acid-derived moiety. This kind of compound may be formed using as the starting acid a polycarboxylic acid, for example a dicarboxylic acid or a dimer or trimer acid. Suitably, the number of moles of acid and alkanolamine which are reacted is controlled such that the resulting ester contains at least one free carboxylic functional group in the acid derived-moiety. For example, if an acid having two carboxyl functions is used, such as a dicarboxylic or dimer acid, the mole ratio could be about 1:1.

In the case that the ester contains at least one free carboxylic group in the acid moiety, it may be used as is or it may be derivatised further to enhance its properties. The kind of compound used to derivatise the ester further usually depends upon the kind of acid used initially to form the ester and the properties of the ester it is desired to influence. For example, it is possible to increase the fuel-solubility of the ester by introducing into the ester molecule a fuel-solubilizing species. As an example of such, long-chain alkyl or alkenyl groups may be mentioned. To this end the ester may be reacted with an alcohol, ROH or an amine, RNH₂ in which R is alkyl or alkenyl having up to 30 carbon atoms, for example 4 to 30 carbon atoms. The number of carbon atoms in the alkyl or alkenyl group may depend upon the number of carbon atoms in the ester itself. These compounds react with the free carboxylic functional group(s) of the ester to form a further ester linkage or an amide linkage. Examples of particular alcohols and amides which may be used include oleyl alcohol and oleyl amine.

Alternatively, it is possible to further derivatise the ester to introduce one or more polar head groups. This has the result of increasing the lubricity enhancing effect which the ester exhibits. This is believed to be due to the polar head group increasing the affinity of the ester to metal surfaces. Examples of compounds which may be used to introduce one or more polar head groups include polyamines (e.g. ethylene diamine and diethylene triamine), alkanolamines such as those described above, monohydric alcohols (e.g. ethanol and propanol) and polyhydric alcohols (e.g. ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, glycerol, arabitol, sorbitol, mannitol, pentaerythritol, sorbitan, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol and 1,2-cyclohexanediol).

Typically, unless the ester is one derived from a dimer or trimer acid, the ester is further derivatised to introduce fuel-solubilising species. Dimer and trimer acid esters tend already to contain in the acid backbone long chain alkyl or alkenyl moieties sufficient to provide adequate fuel-solubility.

While it has been described above that it is the ester which is derivatised further, it is quite possible that the same final species can be formed by first reacting free carboxyl functional group(s) of a polycarboxylic acid to introduce oil-solubilising or polar head groups and then reacting the resultant product with the kind of alkanolamine described above to form the ester. Of course, this assumes that the product formed after being derivatised contains at least one free carboxylic group in the acid-derived moiety such that ester formation with the alkanolamine is still possible. In either case the further derivatives are commercially available or may be made by the application or adaptation of known techniques.

Typically, the concentration of the lubricity enhancing additive in the fuel falls in the range 10 to 1000 ppm, preferably 50 to 500 ppm, more preferably still from 100 to 400 ppm. When mixtures of additives are used the overall additive

concentration falls within the typical range quoted.

The present invention further provides a low sulfur fuel comprising a lubricity enhancing additive as hereinbefore described. Such fuel is formulated by simple mixing of the base fuel and the additive in the desired proportions. The base fuel may be a middle distillate fuel or a bio-diesel fuel as described above. For the sake of convenience, the additive may be provided as a concentrate for dilution with fuel. Such a concentrate forms part of the present invention and typically comprises from 99 to 1% by weight additive and from 1 to 99% by weight of solvent or diluent for the additive which solvent or diluent is miscible and/or capable of dissolving in the fuel in which the concentrate is to be used. The solvent or diluent may, of course, be the low sulfur fuel itself. However, examples of other solvents or diluents include white spirit, kerosene, alcohols (e.g. 2-ethyl hexanol, isopropanol and isodecanol), high boiling point aromatic solvents (e.g. toluene and xylene) and cetane improvers (e.g. 2-ethyl hexylnitrate). Of course, these may be used alone or as mixtures.

The concentrate or fuel may also contain other fuel additives in the appropriate proportions thereby providing a multifunctional fuel additive package. Examples of conventional fuel additives which may be used include fuel stabilisers, dispersants, detergents, antifoams, cold flow improvers, cetane number improvers, antioxidants, corrosion inhibitors, antistatic additives, biocides, dyes, smoke reducers, catalyst life enhancers and demulsifiers. The total treat rate for multifunctional formulations containing the lubricity enhancing additive compounds described is typically 200 to 2000 ppm, more usually 300 to 1200 ppm.

The invention also provides a method of reducing fuel pump wear in an engine which operates on a low sulfur-content fuel by using the low sulfur-content fuel described herein. The fuel may be used to reduce wear in rotary and in-line fuel pumps, for example as found in diesel engines, or in fuel transfer pumps. The latter are positioned between the fuel tank and the high pressure fuel pump. The fuel is particularly well suited for reducing wear in fuel injector pumps. The fuel may also be used to reduce wear in the latest fuel injector units which combine fuel pump and injector mechanisms. The invention is particularly well-suited to the operation of diesel and jet engines.

The present invention is illustrated in the following Example.

Example

The efficacy of a number of diesel fuels was assessed using the Scuffing BOCLE (ball-on-cylinder lubricity evaluator) test. This test is a modification of the standard aviation BOCLE test (ASTM method D5001: "Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)", ASTM Standards, Section 5, Vol 3, 1993) in which a load of 1 kg is applied to a fixed ball in contact with a rotating cylinder lubricated by the test fuel. In this standard test fuel lubricity is assessed by measuring the size of the wear scar on the fixed ball resulting from the constant load contact with the cylinder. However, the standard BOCLE test suffers the disadvantage that the applied load is not high enough to model the type of severe wear failure that occurs in the field, for example in fuel injector pumps.

The Scuffing BOCLE test offers the advantage over the standard test of allowing discrimination and ranking of fuels of differing lubricity. The Scuffing test also simulates more closely the severe modes of wear failure encountered in fuel pumps than other fuel lubricity tests which run under mild wear conditions. The Scuffing BOCLE test therefore provides results which are more representative of how the fuel would behave in service.

In the Scuffing BOCLE test a load (0.25-8.0 kg) is applied to a fixed ball in contact with a rotating cylinder. The ball and cylinder are made of a standard grade steel. The cylinder rotates at 290 rpm. Since the temperature of the lubricating fuel can have a marked effect on the scuffing load, this is carefully controlled at 25°C. A nitrogen atmosphere is used to blanket the ball-on-cylinder assembly. Following a one minute run-in period the load is applied to the ball for two minutes. After this run, the ball is removed from the assembly and the type and size of wear scar examined by microscope. Further runs are then carried using increased applied loads in a stepwise manner until scuffing wear failure occurs. The load at which wear failure occurs is referred to as the scuffing load and is a measure of the inherent lubricity of the fuel. The scuffing load is primarily identified by the size and appearance of the wear scar on the ball, which is considerably different in appearance to that found under milder non-scuffing conditions. Fuels giving a high scuffing load on failure have better lubricating properties than fuels giving a low scuffing load on failure.

The base fuel used was a Class 2 Scandinavian diesel fuel. This is a diesel fuel having a sulfur content of 0.005% by weight. The composition and distillation profile of this fuel are shown below.

Density at 15°C (IP 160), g/ml	0.8160
Paraffins, %vol	89.6
Olefins, %vol	0.7
Aromatics, %vol	9.7

(continued)

Distillation Characteristics (IP 123)	
Initial B.P., °C	184
5%	200
10%	204
20%	212
30%	217
40%	223
50%	228
60%	235
70%	243
80%	251
90%	263
95%	269
Final B.P., °C	290
Recovered, %	99
Residue, %	1
Loss, %	0

The table below shows the Scuffing BOCLE test results for a number of diesel fuels. Samples B-E are fuels in accordance with the present invention. Sample A is included for comparison.

Additive	Concentration (ppm)	Scuffing load (kg)
A. None	-	2.7
B. Ester: Dimer acid + TEA	200	7.4
C. Ester: Dimer acid + TIPA	200	5.6
D. Ester: Dimer acid + EDA.4PO	200	5.7
E. Ester: Dimer acid + DETA.5PO	200	5.7
F. Ester: Dimer acid + EDA.9PO	200	4.8
G. Ester: Dimer acid + EDA.9PO then DETA	200	5.1
H. Ester: Dimer acid + EDA.9PO then TETA	200	5.9

The dimer acid used is formed from oleic and linoleic acids and is commercially available from Union Camp under the name Unidyme 22.

In the table above:

TEA stands for triethanolamine;

TIPA stands for triisopropanolamine;

EDA stands for ethylene diamine;

EDA.XPO indicates that each mole of EDA is reacted with X moles of propylene oxide;

DETA stands for diethylene triamine;

TETA stands for triethylene tetramine;

DETA.5PO indicates that each mole of DETA is reacted with five moles of propylene oxide.

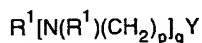
In runs B-E the mole ratio of dimer acid: alkanolamine was in each case 1:2. In runs F-H the mole ratio of dimer

acid:alkanolamine was 1:1. In runs G and H the ester is derivatised further by reaction with DETA and TETA respectively.

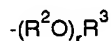
These results clearly demonstrate the improvement in lubricity of diesel fuels in accordance with the present invention. The base fuel used has a very low inherent lubricity giving a low scuffing load result of 2.7 kg. The addition of 200 ppm of additive in accordance with the present invention leads to a significant improvement in lubricity performance exhibited as a higher scuffing load on failure. As can be seen from the table above the additives used in accordance with the present invention lead to a scuffing load on failure which is significantly higher than the load on failure observed for the base fuel.

10 Claims

1. Use of a carboxylic acid ester of an alkanolamine as an additive for improving the lubricity of a low sulfur-content fuel.
2. Use according to claim 1, wherein the fuel is a diesel fuel, jet fuel or bio-diesel fuel.
3. Use according to claim 1 or 2, wherein the sulfur content of the fuel is 0.2% by weight or less.
4. Use according to any one of claims 1 to 3, wherein the acid has from 10 to 60 carbon atoms.
5. Use according to any one of claims 1 to 4, wherein the acid is a dimer acid of oleic and linoleic acids.
6. Use according to any one of claims 1 to 5, wherein the alkanolamine is of formula:



in which p is 2 to 10, q is 0 to 10, Y is $-N(R^1)_2$, 4-morpholinyl or 1-piperazinyl N-substituted by a group R^1 or a group $-[(CH_2)_pN(R^1)]_qR^1$ in which p and q are as defined above, and each substituent R^1 is independently selected from alkyl groups having from 1 to 6 carbon atoms and a group of formula:



in which r is 0 to 10, R^2 is an alkylene group having from 2 to 6 carbon atoms and R^3 is a hydroxyalkyl group having 2 to 6 carbon atoms, provided at least one group R^1 is $-(R^2O)_rR^3$.

7. Use according to claim 6, wherein the alkanolamine is triethanolamine or triisopropanolamine or ethylene diamine or diethylene triamine in which each nitrogen atom is substituted by hydroxyethyl or hydroxypropyl groups.
8. Use according to claim 6, wherein the alkanolamine is aminoethylpiperazine, bis-(aminoethyl)piperazine or morpholine, N-substituted by an hydroxypropyl group.
9. Use according to any one of claims 1 to 8, wherein the ester contains at least one free carboxyl functional group in the acid-derived moiety.
10. Use according to claim 9, wherein the ester is further derivatised by reaction with a compound which introduces a fuel-solubilising species into the ester molecule or by reaction with a compound which introduces a polar head group into the ester molecule.
11. Use according to any one of claims 1 to 10, wherein the ester is present in the fuel at a concentration of from 10 to 1000ppm.
12. A low sulfur-content fuel comprising a carboxylic acid ester as defined in claim 1 or in any one of claims 4 to 10.
13. An additive concentrate for use in low sulfur-content middle distillate fuel comprising from 99 to 1% by weight of a carboxylic acid ester as defined in claim 1 or in any one of claims 4 to 10, and from 1 to 99% by weight of solvent or diluent for the ester which solvent or diluent is miscible and/or capable of dissolving in the fuel in which the

concentrate is to be used.

14. A method of reducing fuel pump wear in an engine which operates on a low sulfur fuel which comprises using a fuel as defined in claim 12.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 8194

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	FR 1 399 466 A (ESS0) * page 3, column 1, line 42; claims A1,A6,B13,B14 * * page 3, column 2, paragraph 3 * * page 4, column 1, paragraph 2 * ---	1-6, 11-14	C10L1/22
X	US 5 352 377 A (BLAIN ET AL.) * column 4, line 44 - column 5, line 26 * * abstract * ---	1-4,6-9, 11-14	
X	EP 0 555 006 A (SLOVNAFT) * example 2 * ---	1,4,6-9, 11-13	
P,X	WO 95 33805 A (EXXON) * page 15 * ---	1-4,6,7, 10-14	
X	US 2 854 324 A (SHEN ET AL.) * the whole document * ---	13	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	US 3 088 815 A (HANEY ET AL.) * the whole document * ---	13	C10L
X	US 2 854 323 A (SHEN ET AL.) * the whole document * ---	13	
X	US 3 183 070 A (UDELHOFEN) * the whole document * ---	13	
X	US 3 117 931 A (WESTLUND ET AL.) * the whole document * ---	13	
X	EP 0 464 489 A (BASF) * the whole document * ---	13	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 March 1997	Examiner De La Morinerie, B
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

EPO FORM 150 (04.92) (P/CN)



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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 8194

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 085 803 A (NIPPON OIL AND FATS) * the whole document * -----	13	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 March 1997	Examiner De La Morinerie, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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